Journal of Electron Devices, Vol. 15, 2012, pp. 1215-1224

© JED [ISSN: 1682 -3427]

Journal of Electron Devices
www.jeldev.org

OPTICAL AND ELECTRICAL PROPERTIES OF NITROGEN DOPED ZnO THIN FILMS PREPARED BY LOW COST SPRAY PYROLYSIS TECHNIQUE

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Received 5-07-2012, revised 14-07-2012, online 20-08-2012

ABSTRACT

Nitrogen doped p type ZnO films are prepared by a simple and low cost spray pyrolysis technique for various precursor solution concentration with air as carrier gas. The optical constants such as refractive index (n) and extinction coefficient (k), band gap, and the electrical properties of the prepared thin films are measured. The band gap of the thin films is calculated using the optical spectrum which is in the range of 3 eV to 3.2 eV. From the electrical properties, it is found that the electrical resistivity of the thin films is in the range of 1.649-2.063 Ωcm. The Hall Effect measurement confirms that the grown films were p type.

Keywords : ZnO:N ; Spray pyrolysis; Electrical properties; Optical properties; P type ZnO; Optical Constants

I. INTRODUCTION

Thin films of transparent semiconducting oxides have many applications in optics, electronics and energy conversion devices such as flat panel displays, transparent electrodes, smart windows for solar cells and polymer based electronic devices [1-3]. ZnO is a wide bandgap(3.3 eV) transparent semiconducting oxide material with large free exciton binding energy (60 meV) which can be used for short wavelength light emitting devices and laser diodes.[4-8]. The advantage of ZnO is that it can be prepared as n type and also as p type by proper doping. There are enormous works on n type ZnO transparent conducting oxides available in literature [9-16]. On the other hand the fabrication of p type ZnO is very difficult due to its self compensation of shallow acceptor resulting from various naturally occurring donor defects such as oxygen vacancies or interstitial Zinc[17,18]. One of the methods of fabricating of p type ZnO is doping with Nitrogen and they are prepared by various methods[19-23]. But there are only few literatures are available for the measurement of optical constants of Nitrogen doped ZnO.

Optical properties of thin films are very important for the designing of solar cells and optoelectronic devices. In particular, the information about optical constants such as refractive index(n) and the extinction coefficient (k) plays a vital role in the designing of optoelectronic devices. They are extensively used for characterization of composition of material over a wide range of wavelength in optic devices [24]. Taking this in to consideration it is decided to fabricate p type ZnO doped with nitrogen by simplified spray pyrolysis [25] by varying the concentration of the precursor solution. The optical constants of the as grown films are measured from the transmission spectra and the electrical properties of the grown films are also studied to confirm the p type.

II. EXPERIMENTAL DETAILS:

ZnO doped with Nitrogen (ZnO:N) thin films are formed for different precursor solutions by varying the molar concentration. Zinc Acetate and Ammonium Acetate are used as the source for Zn and N. The ratio between the Zn and N is kept at 1: 3 for all samples. The precursor solutions are prepared for 0.1, 0.15, 0.2 and 0.25 molarities. The prepared precursor solutions are then sprayed intermittently by means of a perfume atomizer on the pre-heated glass substrates of dimensions $25 \times 25 \times 1.35$ mm^3 with spray interval of 10 seconds. The temperature of the substrate is maintained at 400 ± 5 º C.

The prepared samples are named as A,B,C and D for the molar concentrations of 0.1,0.15,0.2 and 0.25 respectively. The optical studies were carried out by Perkin Elmer Lambda 35 UV-VIS-NIR double beam spectrophotometer . The electrical studies such as resistivity, hall mobility and charge density are done by Ecopia HMS 5000 Hall Effect measurement system. The thickness of the grown films are measured by Surftest SJ 301 profilometer and they are found to be 806 nm ,761nm ,711 nm, and 924 nm for the samples A,B,C and D.

III. RESULTS AND DISCUSSION

III.1. Electrical Properties

The electrical properties of ZnO:N films deposited for various concentration is given in Table 1. The resistivity decreases with the increase of molarity of the solution and it varies with the thickness of the thin films. The Hall mobility of the grown films is decreased when the resistivity decreases [20].

It is clear from the Table 1 that the thickness of the films plays a vital role to determine the resistivity and mobility even though the precursor is increased. From the table, regardless of heavy Nitrogen concentration, the resistivity increases due to rise in thickness which results increase in the mobility for the sample D. This shows a typical semiconductor behavior. The carrier concentration increases with the increase in precursor concentration and decrease in the thickness. The thickness of the grown films increases with decrease in carrier concentration decreases even the precursor concentration increases. On comparison with the other methods [23, 26], it is observed that the resistivity, carrier concentration and the carrier mobility are low and it may be the result of preparative conditions. The electrical properties of the as grown ZnO:N films are compared with pure ZnO [27], the type conversion is occurred and the carrier concentration is slightly increased due to the addition of Nitrogen source.

From the above results, the p type conductivity of ZnO thin films can be increased by addition of more Nitrogen ions and it can be limited by the thickness.

Table 1: Electrical Properties of ZnO:N thin films

Sample	**Thickness (nm)**	**Resistivity Ω cm**	**Carrier Density(cm^{-3})**	**Type**	**Mobility cm^2/Vs**
A(0.1 M)	806	2.063×10^{-2}	0.908×10^{15}	P	14.17
B(0.15 M)	761	1.856×10^{-2}	1×10^{15}	P	11.48
C(0.2 M)	711	1.649×10^{-2}	1.13×10^{15}	P	9.066
D(0.25 M)	924	1.876×10^{-2}	0.9×10^{15}	P	11.734

III.2. Optical Properties

Optical Constants of the prepared films are measured using UV transmission spectrum. The Fig. 1 shows that the transmission spectrum of the films of various solvent ratios.

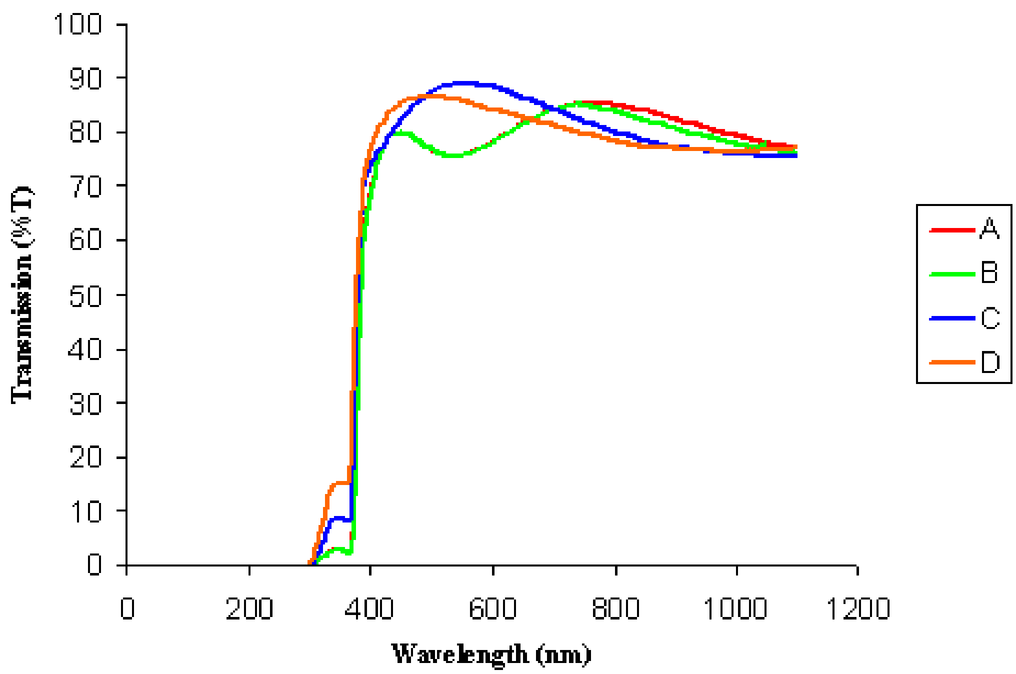

Figure 1: Transmission Spectrum of grown ZnO: N films

From the transmission spectrum it is clear that the transmission of the films decreases with increase of precursor solution concentration. Sample C exhibits maximum transparency of about 90%. All other samples are having over 80% transparency in the visible region and it continuous up to near infrared region. The transparency is in good agreement with the Nitrogen doped ZnO in earlier report [28].

The optical band gap of the deposited films is determined by the following equation[29].

$$(\alpha h\nu) = A(h\nu - Eg)^m \quad (1)$$

where A is an energy independent constant, m is a constant that determine the optical transmission type and Eg is the Energy gap. A plot of $(\alpha h\nu)^2$ versus hν is shown in Fig 2.

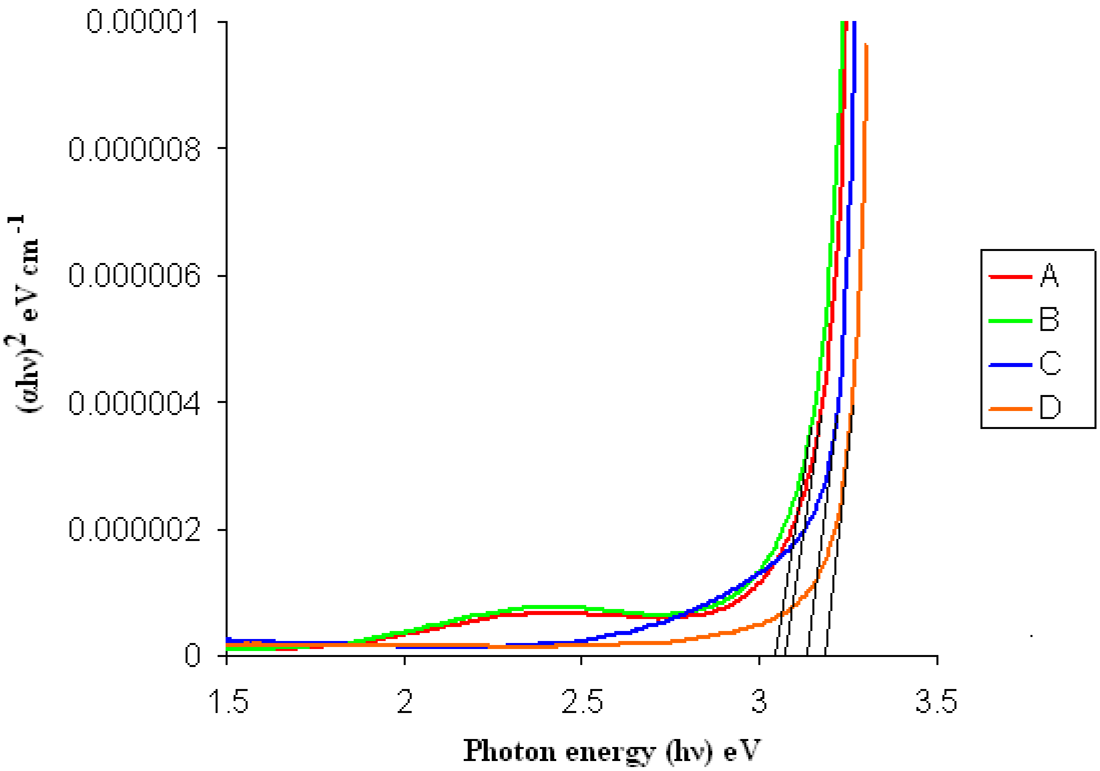

Figure 2: Optical bandgap of the ZnO:N films

The band gap of the grown films increases with increase in precursor concentration and the values are found to be in the range of 3.1eV, 3 eV, 3.18 eV and 3.2 eV for the samples A, B, C and D respectively. These values are well matched with the previous study [30]. The decrease in the band gap of sample B may be due to crystalline imperfections.

The measurement of refractive index (n), extinction coefficient (k) and complex dielectric function is very important to characterize the optical properties of the solid materials. The normal incidence reflectivity R is given by [31].

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (2)$$

where n is the refractive index and k is the extinction coefficient (k=$\frac{\propto \lambda}{4\pi}$). The values of n and k are calculated using the above equations. The refractive index dependence of photon energy is plotted in Fig .3.

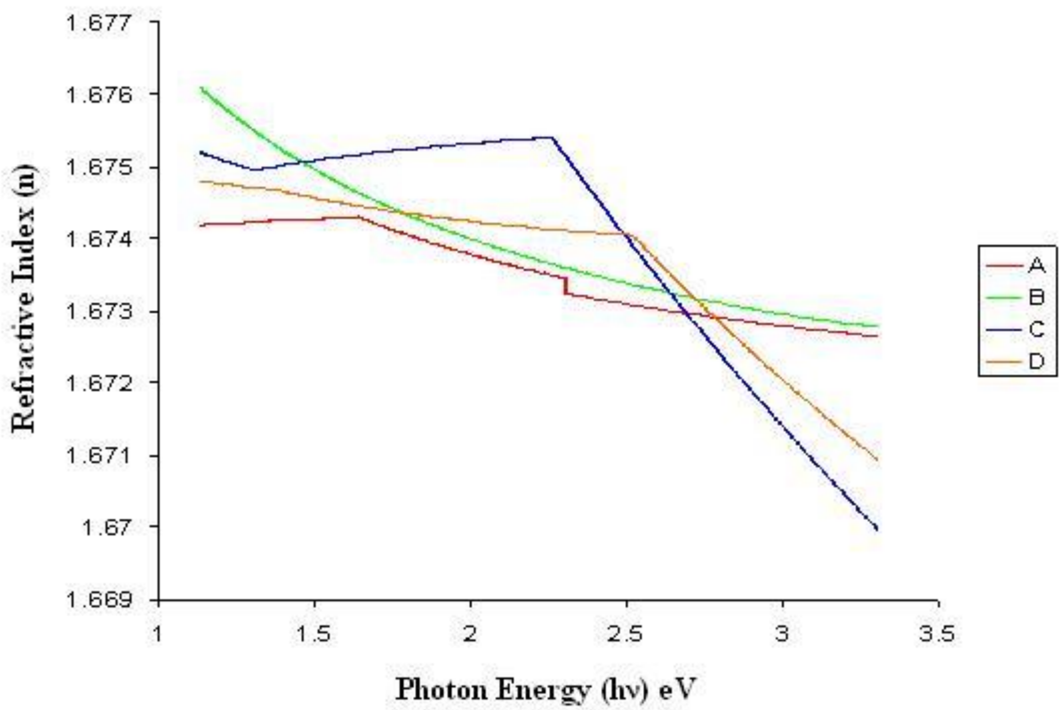

Figure 3: Refractive index vs Photon Energy

The calculated refractive index of the grown films decreases with precursor solution concentration. Compared with the values reported in [32], the obtained values of refractive index are low and it may be due to the methodology of sample preparation and the substrate. It is seen that, the values of n are in the range of 1.670 to 1.676. The band gap for the samples increases with decrease in refractive index [33].

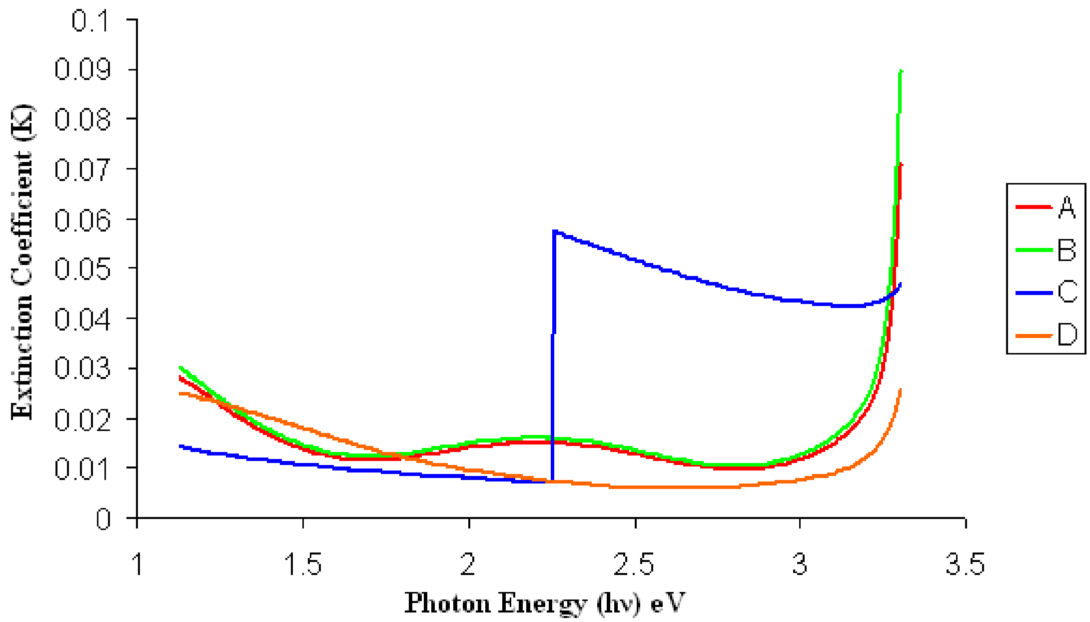

Figure 4: Extinction Coefficient(k) vs Photon Energy

The extinction coefficient (k) plot against the photon energy in Fig. 4 shows that the grown films are not strong absorbing medium [32] since it has the values of low range. Stronger absorbing medium shows higher extinction coefficient

The optical conductivity is measured using the following formula [34]

$$\sigma = \frac{\alpha n c}{4\pi} \tag{3}$$

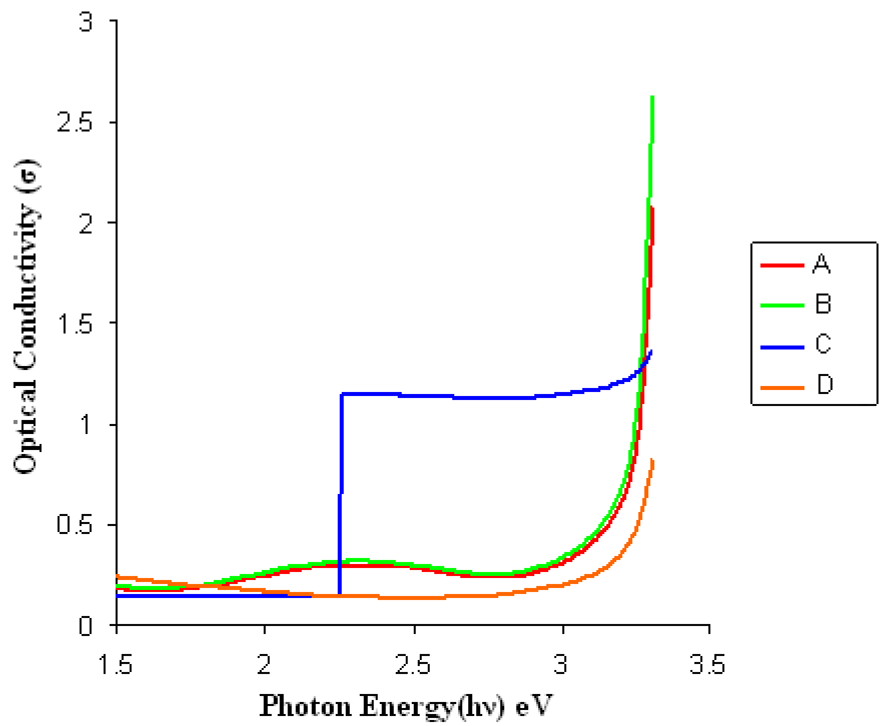

Figure 5: Optical Conductivity(σ) vs Photon Energy

From Fig. 5 it is clear that the optical conductivity increases with the increase of solution concentration. This may be due to the addition of charge carriers in the precursor solution.

The imaginary ε_i and real $\varepsilon_r$parts of the dielectric constants are plotted as a function of photon energy is shown in Fig 6 and in Fig 7. The values of ε_r increases with incident photon energy and ε_i decreases with it.

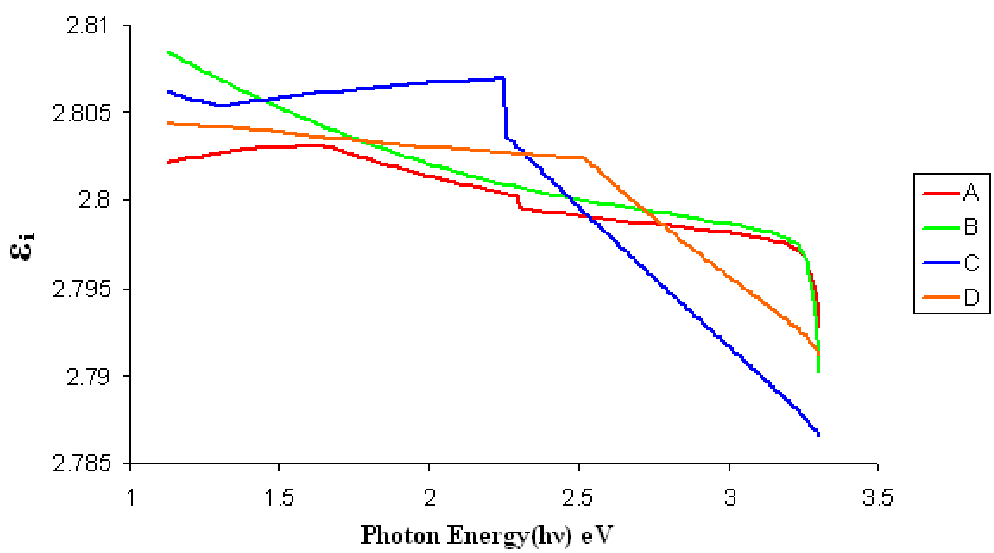

Figure 6: Dielectric Constant Imaginary (εi) vs Photon Energy

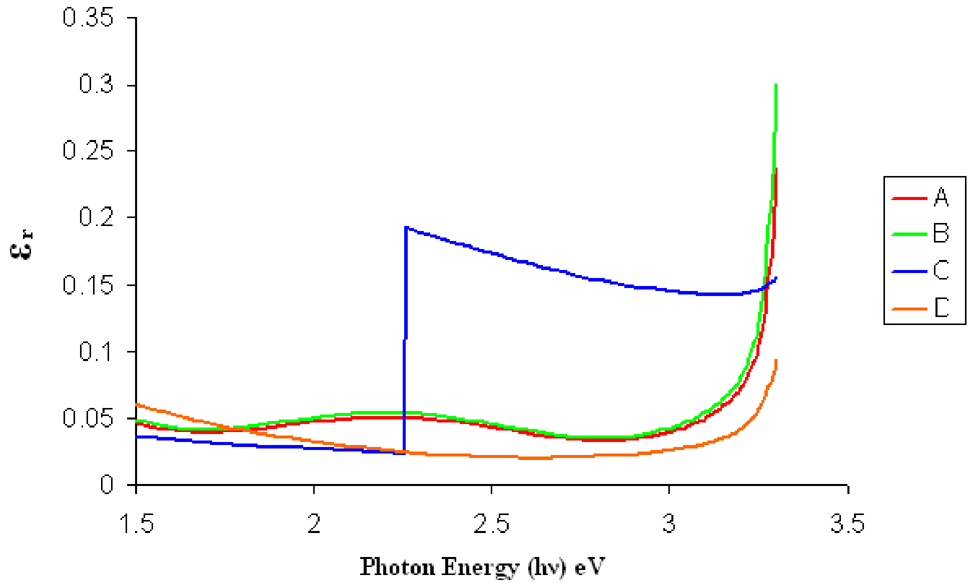

Figure 7: Dielectric Constant Real (εr) vs Photon Energy

It is clear from the plots of dielectric constant that the real and imaginary parts of the dielectric constants can be altered by varying the precursor solution. A slight modification in the precursor solution attributes major variation in the dielectric constant.

IV. CONCLUSION

P type transparent conducting oxide ZnO:N thin films have been prepared by a low cost spray pyrolysis technique. It can be seen that the change of solution concentration plays a vital role in the change in electrical and optical properties of the thin films. The electrical studies of the films confirm that they are p type and have the resistivity in the range of 1.649-2.063 Ωcm. The refractive index values of the grown film are in the range of 1.670 to 1.676. The other optical constants such as extinction coefficient, dielectric constants and the optical conductivity are also calculated and it shows a significant variation by varying the concentration of the precursor solution. From the observed values of electrical and optical properties of the as grown films, it is seen that the values are low compared to other methods and it can be used to design optoelectronic devices.

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